

Geometry optimization, HOMO and LUMO energy, molecular electrostatic potential, NMR, FT-IR and FT-Raman analyzes on 4-nitrophenol

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Abstract. In the present work, the equilibrium geometry, HOMO-LUMO energy gap, chemical shifts, vibrational frequencies, IR and Raman intensities and thermodynamic parameters of 4-nitrophenol molecule was calculated using the methods of HF and DFT/B3YLP employing 6-311+G basis set. Theoretically calculated geometrical parameters such as bond length and bond angle were compared with the corresponding experimental X-ray diffraction values. The highest occupied (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the 4-NP molecule have been calculated. The study was extended to calculate the energy gap, ionization potential, electron affinity and chemical hardness. HOMO-LUMO electronic transition of 3.76 eV is obtained from the contribution of the bands. The reacting electrophilic and nucleophilic sites of the molecule were analyzed with the help of molecular electrostatic potential (MEP) surface analysis. The different proton and carbon environment of the grown crystal was analyzed by ¹H and ¹³C NMR analyses. All vibrational frequencies were assigned and compared with the calculated frequencies in detail.

1 Introduction

The crystal structures of organic compounds are very hard to predict because of their weak intermolecular interactions [1]. However the study on organic crystal structures becomes more important to researchers and industrialists since understanding the complete structure of the compound will assist in synthesizing the materials with particular properties. In recent years, electron donor-acceptor (EDA) complexes play an important role in the field of organic semiconductors, photocatalysts and dendrimers [2–4]. 4-nitrophenol (4-NP) compound with push-pull electron interaction is an interesting intramolecular charge transfer system. 4-NP is a nitrated phenolic compound that has an nitro group at the opposite position of hydroxyl groups on the aromatic ring. 4-NP single crystals contain chains of hydrogen bonded molecules. The benzene ring is planar however the nitrogen and oxygen atoms are shifted from the benzene ring [5]. The purpose of the present work is to apply ab initio molecular orbital (MO) method to interpret the geometry of 4-NP crystals. Gaussian calculates the energies, molecular structures, vibrational frequencies of molecular systems, along with numerous molecular properties derived

from these basic computation types [6]. Hartree-Fock is the basic ab initio model. Many quantum chemical calculations begin with the Hartree-Fock level of theory with subsequent corrections for coulombic electron-electron repulsions [7]. Generally the results obtained using ab initio methods are comparable with the results obtained with hybrid DFT/B3YLP because it uses corrections for both gradient and exchange correlations. The ab initio or density functional theory requires a basis set specification since it describes the shape of atomic orbitals. In this investigation, we have calculated the structural stability of the optimized geometry, HOMO-LUMO energy gap, NMR chemical shifts and the vibrational assignments of the title compound in the ground state with medium size basis set 6-311+G to produce qualitatively reliable results.

2 Experimental

X-ray diffraction intensity data were collected for 4-nitrophenol compound using Bruker SMART Apex II single crystal X-ray diffractometer equipped with graphite monochromated MoK α ($\lambda = 0.7103$ Å) radiation and CCD detector. The infrared absorption spectrum of the grown 4-NP crystal has been recorded in the range

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ORIGINAL ARTICLE

Cross-Layer Design Approach for Power Control in Mobile Ad Hoc Networks



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KEYWORDS

RSS;
AODV;
CLPC

Abstract In mobile ad hoc networks, communication among mobile nodes occurs through wireless medium. The design of ad hoc network protocol, generally based on a traditional “layered approach”, has been found ineffective to deal with receiving signal strength (RSS)-related problems, affecting the physical layer, the network layer and transport layer. This paper proposes a design approach, deviating from the traditional network design, toward enhancing the cross-layer interaction among different layers, namely physical, MAC and network. The Cross-Layer design approach for Power control (CLPC) would help to enhance the transmission power by averaging the RSS values and to find an effective route between the source and the destination. This cross-layer design approach was tested by simulation (NS2 simulator) and its performance over AODV was found to be better.

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1. Introduction

A mobile ad hoc network is a collection of wireless nodes that can transfer data without the use of network infrastructure or administration. Such networks have many potential applications, including in disaster mitigation, defense, health care, academia and business. In such a network, every node acts both as a host and a router.

A major limitation with mobile nodes is that they have high mobility, causing links to be frequently broken and reestablished. Moreover, the bandwidth of a wireless channel is also limited, and nodes operate on limited battery power, which will eventually be exhausted. Therefore, the design of a mobile ad hoc network is highly challenging, but this technology has

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Plasmon-Assisted Enhancement and Tuning of Optical Properties in β -In₂S₃ Quantum Dots

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Abstract Exciton-plasmon coupling can significantly modify the spectral response of semiconductor quantum dots in a metal nanoparticle-semiconductor complex system. β -In₂S₃ quantum dots of size ~ 3 nm and Ag nanospheres of size ~ 100 nm were synthesized by chemical route and coated over glass substrates. In the strong coupling regime, the plasmons are shown to mediate indirect Coulomb interaction between the quantum dots. In the proximity of Ag plasmons, the excitonic binding energy of the β -In₂S₃ quantum dots increases by ~ 500 meV, indicating that the interaction potential between the quantum dots is positive and repulsive in nature. This interaction also leads to strong coupling of the defect levels in the SQD complex. The defect emission wavelength can be enhanced by an order of 10^2 or shifted from red region (~ 650 nm) to green (~ 550 nm) by controlling the plasmon-induced defect level coupling. The experimental observation demonstrates one of the theoretically predicted consequences of exciton-plasmon interaction. This work demonstrates the possibility of harnessing the potential of the two complementary systems (semiconductor quantum dots and metal nanoparticles) to achieve controllable emission and absorption properties for fabrication of nano plasmonic devices.

Keywords Quantum dots · Semiconductor · Plasmons · Emission · Absorption

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Introduction

Light matter interaction in nanostructures such as metal/semiconductor or metal/dielectric structures is an active area of research with enormous potential in photonic device and biomedical applications [1]. Metal nanoparticles (MNPs) exhibit very strong plasmon resonances, leading to electric fields of high intensity around them with an exponentially decaying intensity away from the MNP surface in the nanometer range. When such plasmonic structures are in close proximity with semiconductor quantum dots (SQD) which have high surface density of states, one can achieve controllable emission and absorption properties and their spectral response will be modified considerably. The near-field interaction between the SQDs and MNPs influences the molecular dynamics in the particles, leading to enhanced light matter interaction. Such a plasmon-mediated light matter interaction is evident from the observations of increase/decrease in energy transfer rates, enhancement/suppression of radiative, non-radiative emission intensity, and modified spectral profiles of either metal nanoparticle, SQD, or both.

The MNP-SQD super structures also exhibit several interesting phenomena such as resonant energy transfer [2], spin plasmon interaction [3], transportation of entangled photons by plasmons [4], nonlinear Fano effect, ultrafast control of light matter interaction [5], controlled slow light [6] etc. These systems have been studied for suitability in several applications such as single-photon source [7], single-photon transistor [8], and quantum information processing [9]. The physics of these structures has been studied theoretically in an extensive manner, but there are only very few experimental demonstrations of the theoretically predicted phenomena.

Semiconductor quantum dots exhibit size-dependent optical absorption and emission properties as they have discrete energy levels unlike their bulk counterpart. The electronic

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A Survey Of Big Data Analytics in Healthcare and Government*J.Archenaa¹ and E.A.Mary Anita²**¹Research Scholar, AMET University, Chennai, ²S.A.Engineering College, Chennai
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Abstract

This paper gives an insight of how we can uncover additional value from the data generated by healthcare and government. Large amount of heterogeneous data is generated by these agencies. But without proper data analytics methods these data became useless. Big Data Analytics using Hadoop plays an effective role in performing meaningful real-time analysis on the huge volume of data and able to predict the emergency situations before it happens. It describes about the big data use cases in healthcare and government.

Keywords: Big Data, Hadoop, Healthcare, Map-Reduce

1. Introduction

The healthcare industry has generated large amount of data generated from record keeping, compliance and patient related data. In today's digital world, it is mandatory that these data should be digitized. To improve the quality of healthcare by minimizing the costs, it's necessary that large volume of data generated should be analysed effectively to answer new challenges. Similarly government also generates petabytes of data every day. It requires a technology that helps to perform a real time analysis on the enormous data set. This will help the government to provide value added services to the citizens. Big data analytics helps in discovering valuable decisions by understanding the data patterns and the relationship between them with the help of machine learning algorithms⁽¹⁾. This paper provides an overview of big data analytics in healthcare and government systems. It describes about big data generated by these systems, data characteristics, security issues in handling big data and how big data analytics helps to gain a meaningful insight on these data set.

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Analysis on the Growth and Characterization of a Non-linear Optical Single Crystal: L-Cystine Dihydrobromide

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Nonlinear optical single crystals of L-cystine dihydrobromide (LCHB) have been grown by slow evaporation method. Single crystal X-ray diffraction analysis revealed the crystal system and lattice parameter values. Powder X-ray diffraction analyses have been carried out and the diffraction patterns have been indexed. Fourier transform infrared (FTIR) analysis confirms the various functional groups present in the grown crystal. The thermal behavior of the grown crystal was investigated by DTA and TGA analysis. The optical properties of the crystals were determined using UV-Visible transmittance spectrum. The dielectric constant and dielectric loss of the crystal are studied as a function of frequency for various temperatures. The SHG efficiency of the crystal is studied using the Kurtz and Perry technique.

Keywords: growth from solution, x-ray diffraction, infrared spectra, optical transmission spectrum

1. Introduction

L-cysteine [$C_3H_7NO_2S$] is the simplest amino acid and it has centre of chirality and is optically active. L-cysteine can exist as neutral molecule in the gas phase; it exists as a Zwitterion in solution as well as in solid state. L-cysteine crystallizes in non-centrosymmetric space group making it a potential candidate for piezoelectric and non-linear applications. L-cysteine exist as a dipolar ion in solid state in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. In addition, thiol group is present in aqueous solution of L-cysteine. Due to this dipolar nature, L-cysteine has a high melting point. Another added advantage of L-cysteine is the presence of chromophores namely amino group and carboxyl group which makes it transparent in the UV-Vis region^{1,2}. Thus more emphasis has been given by the scientists to develop non-linear optical crystals in L-cysteine and its analogs. Experiments conducted by Martin et al.³, Loganayaki et al.⁴, Bhagavannarayana et al.⁵, Selvaraju et al.⁶ and Anbuechezhiyan et al.⁷ reveal the suitability of L-cysteine family crystals for their non-linear optical properties and applications. The non-linear optical properties of L-cysteine analogs make them strong candidates to replace KDP for frequency conversion of infrared lasers. All compounds of this class contain optically active carbon atoms and therefore all of them form acentric crystals⁸. The present study deals with L-cystine dihydrobromide (LCHB), one of the non-linear optical crystals belonging to L-cysteine family. The growth of the crystal has been achieved by slow solvent evaporation technique. The grown crystals were characterized by single

crystal XRD analysis, powder XRD, FTIR, thermal analysis, DSC, UV analysis, dielectric and SHG studies.

2. Experimental Procedure

2.1. Crystal growth

L-cystine dihydrobromide ($C_6H_{14}Br_2N_2O_4S_2$) crystals are grown from aqueous solution by slow solvent evaporation technique. The starting materials are L-cysteine and hydrobromic acid. The solution is prepared by dissolving equimolar amount of 2:2 of L-cysteine and hydrobromic acid in double distilled water and the solution is stirred using a magnetic stirrer having hot plate attachment. The mixed solution was slowly heated up to 60 °C and a saturated solution was obtained. This solution is filtered using micro filter paper of 10 µm. The filtered saturated solution is transferred into a petri dish. The prepared solution is allowed to evaporate at room temperature and kept in undisturbed condition. Large size single crystals were obtained due to the collection of monomers at the seed crystal sites from the mother solution, after the nucleation and growth processes were completed. LCHB crystal of dimension about 10 × 10 × 6 mm³ was harvested in a growth period of twenty four days by slow evaporation of the solvent. The photograph of the grown LCHB crystal is shown in Figure 1. During the growth of LCHB, the formation of several fungus like organism in the solution is observed. These organisms start growing on the surface, exposed to atmosphere and subsequently sink into the solution, thereby, contaminate it. Due to this reason,

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